Non-linear Optical Properties of Organic Molecules. Part 20.* Calculation of the Structure, Electronic Properties and Hyperpolarizabilities of Donor–Acceptor Heterocycles containing Sulfur, Oxygen and Nitrogen

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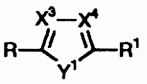
The structures of a donor–acceptor thiophene, furan, pyrrole, thiadiazole, oxadiazole and the three ring tautomers of the corresponding triazole, have been calculated using the *ab initio* 3-21G basis set to give a reasonable correlation with crystallographic data where available. The non-linear optical properties of these structures have been assessed by calculating their molecular hyperpolarizabilities using a sum-over-states semiempirical approach. The results show that the 1,3,4-thiadiazole, 1,3,4-oxadiazole and 1,3,4-triazole, exhibit much larger dipole moment changes than the corresponding thiophene, furan and pyrrole on excitation, but their calculated hyperpolarizabilities are smaller mainly because of their smaller transition moments.

A considerable research effort is underway in the field of nonlinear optics to find materials which are able to act effectively as second harmonic generators (SHG) or electro-optic modulators (EOM).[1] A large number of organic molecules have been synthesized and evaluated for these applications using electric field induced second harmonic generation in solution and many more have been assessed theoretically by calculating their molecular hyperpolarizabilities using a variety of methods. Previous work has shown that donor–acceptor polyenes have the largest hyperpolarizabilities,[2,3] though these tend to be less stable than the corresponding aromatics such as 4-nitroaniline, because they are easily oxidized in the presence of light. Furthermore, polyenes, in general, readily isomerize from the preferred all-*trans* conformations to the *cis*-form. Modified polyenes such as the related donor–acceptor polythiophenes, polyfurans and polypyrroles also have large hyperpolarizabilities[4] and are more stable, but even here the molecules are liable to isomerize and the presence of the polar groups lowers the ionization potential and hence the stability of the respective heterocyclic ring.

The studies reported here have been carried out to assess the potential of more stable heterocycles such as the donor–acceptor thiadiazoles (**Ia**), oxadiazoles (**Ib**) and triazoles which can exist in three distinct tautomeric forms (**Ic**–**e**). As in previous studies,[4] the dimethylamino- and nitro- groups were selected as examples of typical donors and acceptors and positioned at opposite sides of the respective molecule and the structures fully optimised. Furthermore, although a previous study has explored the hyperpolarizabilities of the related thiophene (**If**), furan (**Ig**), pyrrole (**Ih**) and *N*,*N*-dimethyl-4-nitroaniline (**II**), empirical structures were adopted for calculation.[4] In the present work, the structures of these systems have been fully optimized and the resulting hyperpolarizabilities re-evaluated and compared with those of the diazoles (**Ia**) and (**Ib**) and the triazoles (**Ic**–**e**).



I

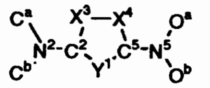
a R = NMe_2; R^1 = NO_2; Y^1 = S; X^3 = X^4 = N
b R = NMe_2; R^1 = NO_2; Y^1 = O; X^3 = X^4 = N
c R = NMe_2; R^1 = NO_2; Y^1 = NH; X^3 = X^4 = N
d R = NMe_2; R^1 = NO_2; Y^1 = X^3 = N; X^4 = NH
e R = NMe_2; R^1 = NO_2; Y^1 = X^4 = N; X^3 = NH
f R = NMe_2; R^1 = NO_2; Y^1 = S; X^3 = X^4 = CH
g R = NMe_2; R^1 = NO_2; Y^1 = O; X^3 = X^4 = CH
h R = NMe_2; R^1 = NO_2; Y^1 = NH; X^3 = X^4 = CH
i R = R^1 = H; Y^1 = S; X^3 = X^4 = N
j R = NHCOMe; R^1 = SO_2NH_2; Y^1 = S; X^3 = X^4 = N
k R = NHMe; R^1 = OEt; Y^1 = O; X^3 = X^4 = N
l R = NH_2; R^1 = NO_2; Y^1 = X^4 = N; X^3 = NH
m R = NH_2; R^1 = CO_2Et; Y^1 = S; X^3 = C–CN; X^4 = C–Me
n R = CH=CHNMe$_3$; R^1 = NO_2; Y^1 = O; X^3 = X^4 = CH
o R = NMe_2; R^1 = CH=C(CN)(CO_2Me); Y^1 = O; X^4 = CH
p R = CH(CMe$_3$)($OSOC_6H_4$Me); R^1 = NO_2; Y^1 = NMe; X^3 = X^4 = CH

Methods of Calculation

Molecular orbital calculations were carried out on empirical structures for all the heterocycles (**Ia**–**h**) using the 3-21G basis set[5] of the GAMESS program[6] with full optimisation of all bond lengths and angles. The numbering convention adopted is shown in Scheme 1. The optimised structures were then used to calculate both the ground and excited state dipole moments, transition energies, oscillator strengths and molecular hyperpolarizabilities using the CNDOVSB method,[7,8] a sum-over-states procedures (SOS) which has been specifically parameterized for both SHG and EOM applications. As in previous work, 50 excited states were used in the evaluation of the tensor and all 27 components calculated by the CNDOVSB method in the cartesian frame. Two measures of the hyperpolarizability were adopted: (1) where a vector component, β_x, is aligned to lie along the direction of the molecular dipole moment (μ), *i.e.*,

$$\beta_x = \beta_{\mu\mu\mu} + \tfrac{1}{3}\sum_{i \neq \mu} (\beta_{\mu ii} + \beta_{ii\mu}) \qquad (1)$$

and (2) where the quantity, β, is a vector of all the directional components, *i.e.*,



Scheme 1 Numbering convention adopted for the heterocycles **I**

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* Part 19, see reference 19.

Table 1 Geometries of the donor–acceptor heterocycles (**I**) calculated with the 3-21G basis set[a]

Variable	**Ia**	**Ib**	**Ic**	**Id**	**Ie**	**If**	**Ig**	**Ih**
Y^1	S	O	NH	N	N	S	O	NH
X^3	N	N	N	N	NH	CH	CH	CH
X^4	N	N	N	NH	N	CH	CH	CH
Y^1–C^2	1.819	1.371	1.362	1.384	1.322	1.812	1.358	1.353
C^2–X^3	1.305	1.306	1.323	1.325	1.359	1.371	1.378	1.398
X^3–X^4	1.403	1.435	1.410	1.401	1.400	1.411	1.419	1.400
X^4–C^5	1.258	1.260	1.276	1.324	1.291	1.343	1.346	1.364
C^5–Y^1	1.793	1.380	1.377	1.294	1.354	1.796	1.385	1.389
C^2–N^2	1.322	1.317	1.337	1.341	1.336	1.340	1.332	1.351
N^2–C^a	1.476	1.475	1.470	1.463	1.462	1.467	1.463	1.462
N^2–C^b	1.467	1.472	1.459	1.465	1.472	1.468	1.472	1.460
C^5–N^5	1.421	1.408	1.406	1.423	1.428	1.387	1.376	1.368
N^5–O^a	1.231	1.239	1.230	1.255	1.243	1.257	1.263	1.255
N^5–O^b	1.253	1.242	1.261	1.226	1.236	1.254	1.247	1.269
N–H			0.996	0.995	0.993			0.996
Y^1–C^2–X^3	114.6	112.5	110.5	113.7	109.1	111.4	109.7	108.0
C^2–X^3–X^4	111.9	105.1	106.4	102.3	109.3	113.6	106.3	107.4
X^3–X^4–C^5	113.8	106.8	107.0	108.2	101.2	114.1	107.3	107.5
X^4–C^5–Y^1	116.5	113.4	112.1	112.8	117.1	112.8	109.7	108.5
C^5–Y^1–C^2	83.3	102.2	104.0	103.1	103.3	88.1	107.0	108.6
Y^1–C^2–N^2	122.0	120.0	125.3	122.6	126.5	120.6	115.6	123.0
C^2–N^2–C^a	117.4	116.2	117.1	118.3	120.0	118.1	119.4	118.2
C^a–N^2–C^b	121.6	122.9	121.8	122.0	121.7	120.3	121.6	121.4
X^4–C^5–N^5	124.1	128.0	127.8	120.7	120.7	126.4	132.4	131.2
C^5–N^5–O^a	118.4	116.4	118.7	114.5	116.8	117.6	116.2	118.5
O^a–N^5–O^b	126.7	127.2	126.6	127.1	126.2	125.2	125.6	125.1
Dipole moment	8.395	7.568	8.257	3.951	9.677	9.242	8.369	8.458

[a] Bond lengths in angstroms; bond angles in degrees; dipole moments in Debyes.

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}} \qquad (2)$$

The values obtained from the former relate directly to those obtained from experimental electric field induced second harmonic generation in solution, while those from the latter give a measure of the overall hyperpolarizability of a given system. In addition to the frequency dependent values, a static value is also calculated in the absence of the applied frequency to give the quantity β_0 which is an approximate measure of the intrinsic hyperpolarizability of a given molecular system.

Results and Discussion

Molecular Structures.—An examination of the Cambridge Structural Database (CSD)[9] shows few examples of the donor–acceptor heterocycles (**I**) discussed here and an assessment of the accuracy of the theoretical results at the 3-21G level with experimental data is therefore difficult. However, the limited structural data available on the thiadiazoles, shows that substituents, particularly electron attractors, appear to exert a strong influence on the geometry of the heterocyclic ring. Thus in moving from the crystal structure of 1,3,4-thiadiazole (**Ii**)[10] to that of 2-acetamido-1,3,4-thiadiazole 5-sulfonamide (**Ij**),[11] the nominal single and double bonds at the N^3–N^4 and N^4–C^5 positions of the ring shorten in length from 1.38 and 1.31 Å respectively to 1.37 and 1.29 Å, respectively, although the C^2–N^3 bond length of 1.31 Å in the parent appears to be unaffected by the presence of the acetamido-group at the 2-position.

This trend is found also in the calculated results where the more powerful electron attracting nitro-group produces a short C^2–N^3 bond length of 1.26 Å, while the C^5–N^4 distance at 1.31 Å appears to be unaffected by the powerful electron donating dimethylamino-group (Table 1). The calculated S^1–C^2 and S^1–C^5 bond lengths appear to be somewhat overestimated by the 3-21G basis set by comparison with the crystallographic data on the related sulfonamido-derivative (**Ij**)[11] but the angle of 83.3° at sulfur is close to the experimental value of 85.0° in the same structure (**Ij**).[11] There are no suitable examples of donor–acceptor 1,3,4-oxadiazoles for comparative purposes but the calculated bond lengths at O^1–C^2, N^3–N^4 and N^4–C^5 of 1.37, 1.44 and 1.26 Å respectively for 2-dimethylamino-5-nitro-1,3,4-oxadiazole (**Ib**) (Table 1) shows a good fit with those found experimentally for 2-methylamino-5-ethoxy-1,3,4-oxadiazole (**Ik**) at 1.36, 1.44 and 1.26 Å, respectively.[12]

In the triazoles, however, there are a number of examples of donor–acceptor derivatives which appear to exist as the 1,2,4-isomer.[9] A comparison of the calculated structure of 3-dimethylamino-5-nitro-1,2,4-triazole (**Ie**) with the highly resolved crystal structure of the 3-amino-derivative (**Il**)[13] shows a reasonable correlation between the calculated bond lengths and angles and those measured experimentally. For example, the calculated values of 1.32, 1.36 and 1.34 Å for the N^1–C^2, C^2–N^3 and C^5–N^1 bond lengths (Table 1) compare favourably with the experimental values of 1.33, 1.35 and 1.34 Å, respectively.[13] Furthermore, the calculated substituent bond lengths of 1.34 and 1.43 Å for C^2–NMe_2 and C^5–NO_2, are also in good agreement with the measured values of 1.34 and 1.45 Å respectively.

As far as the thiophene (**If**), furan (**Ig**) and pyrrole (**Ih**) are concerned there are few structures containing appropriate donor and acceptor groups. In the former, experimental data are available for 2-amino-3-cyano-5-ethoxycarbonyl-4-methylthiophene (**Im**) where the C^2–C^3, C^3–C^4 and C–NMe_2 bond lengths of 1.38, 1.42 and 1.34 Å, respectively, are similar to those calculated for 2-dimethylamino-5-nitrothiophene at 1.37, 1.41 and 1.34 Å, respectively. In the furans, there appears to be quite a wide variation in the bond lengths of the ring atoms depending on the nature of donor and acceptor groups. For example, the O^1–C^2, C^2–C^3 and C^3–C^4 bond lengths vary from 1.37, 1.44 and 1.46 Å, respectively, in 2-(2-dimethylaminovinyl)-5-nitrofuran (**In**)[14] to 1.34, 1.38 and 1.38 Å, respectively, in 2-dimethylamino-5-(2-cyano-2-ethoxycarbonylvinyl)furan (**Io**).[15] The calculated values of 1.36, 1.38 and 1.42 Å for the same bond lengths respectively (Table 1), therefore, show a reasonable correlation

Table 2 Calculated electronic properties and hyperpolarizabilities of the donor–acceptor heterocycles (I)[a]

Molecule	μ_g	μ_e	\	f	β_0	$\beta_{1.17}$	β_x	β_y
Ia	8.40	15.7	366	0.35	9.29	19.9	15.9	−12.1
Ib	8.20	19.2	328	0.29	6.53	12.7	8.37	−9.51
Ic	9.09	19.2	339	0.31	7.70	15.7	8.68	13.1
Id	3.94	17.1	365	0.11	4.94	9.69	9.69	0.14
Ie	10.8	22.1	303	0.12	2.50	3.86	3.81	−0.64
If	9.86	14.2	411	0.51	14.5	41.2	41.0	3.82
Ig	8.68	16.8	383	0.54	14.3	38.3	38.0	−4.76
Ih	8.82	16.4	390	0.58	15.5	43.6	15.0	−12.9
II	8.81	18.6	333	0.68	13.3	26.7	26.7	0.02

[a] All structures were optimised at the 3-21G level; \ is the transition energy (in nm); f is the oscillator strength; μ_g and μ_e are the ground and first excited state dipole moments at the CNDOVSB level (in D); β_0 and $\beta_{1.17}$ are the vector cartesian components of the hyperpolarizability tensor at zero field and 1.17 eV respectively (in units of 10^{-30} cm^5 esu^{-1}); β_x is the vector component of the hyperpolarizability along the dipole moment and β_x is the vector component in the transverse direction (both at 1.17 eV).

with the experimental data. There are only a small number of relevant structures for the corresponding donor–acceptor pyrroles, though the calculated bond lengths at N^1–C^2, C^3–C^4 and C^4–C^5 of 1.35, 1.40 and 1.36 Å compare reasonably well with those found in the related 1-methyl-2-(*tert*-butyltoluene-*p*-sulfonyl)methyl-5-nitropyrrole (**Ip**) at 1.37, 1.40 and 1.35 Å respectively.[16]

Electronic Properties and Hyperpolarizabilities.—All of the structures considered here show a large change in the magnitude of the dipole moment on excitation to the first excited state (Table 2). The change is largest for the triazole (**Id**) which increases from 3.9 to 17 D, followed by the oxadiazole (**Ic**) and triazole (**Ie**), with each showing an increase of around 11 D and smallest for the thiophene (**If**) which increases by a modest 4.3 D. These increases would strongly suggest that the thiadiazole (**Ia**), oxadiazole (**Ib**) and triazoles (**Ic–e**) would be expected to have large hyperpolarizabilities on the basis of the so-called two-level model[17] which has been used extensively to evaluate many donor–acceptor systems such as *N*,*N*-dimethyl-4-nitroaniline (**II**).[18]

The calculated hyperpolarizabilities of these systems, however, using the vector definition of eqn. (2) at zero frequency to eliminate resonance enhancement effects show all to be inferior to the donor–acceptor thiophene (**If**), furan (**Ig**), pyrrole (**Ih**) and nitroaniline (**II**). Of the triazoles (**Ic–e**), the 1,3,4-isomer (**Ic**) has the largest value and the 1,2,4-isomer (**Ie**) the smallest. This arises because the hyperpolarizability is not only dependent on the change in dipole moment on excitation, but also the magnitude of the transition moment or oscillator strength for the two-level model. Thus although both 1,2,4-triazoles (**Id**) and (**Ie**) show large changes in dipole moment on excitation, their oscillator strengths are relatively small (Table 2).

In the 1,2,4-heterocycles (**Ia–c**), the thiadiazole (**Ia**) is predicted to have a larger hyperpolarizability than the triazole (**Ic**), followed by the oxadiazole (**Ib**) in line with the trends found in the oscillator strengths. However, none of these are comparable to the simple heterocycles (**If–g**) which all show much larger values for both the hyperpolarizability and oscillator strength (Table 2). Furthermore, because the thiophene (**If**), furan (**Ig**) and pyrrole (**Ih**), absorb at longer wavelength than the diazoles (**Ia**) and (**Ib**) or the triazole (**Ic**), they show much larger resonance enhancement effects at an applied field (Ω) of 1.17 eV (1060 nm), through terms such as ($\Omega_{ng} - 2\Omega$), where Ω_{ng} is the transition energy, in the denominator of the expression used to calculate the hyperpolarizability at the SOS level.[7]

Although 2-dimethylamino-5-nitro-1,2,4-thiadiazole (**Ia**) shows a comparable frequency dependent hyperpolarizability to *N*,*N*-dimethyl-4-nitroaniline (**II**), when the tensor is evaluated along the direction of the molecular dipole moment [eqn. (1)], the value falls. In the simple heterocycles **If** and **Ig** and the aniline **II**, the charge transfer axis on excitation lies between the donor and acceptor groups along the direction of the dipole moment. When the tensor is rotated from the cartesian reference frame along the direction of the dipole moment almost all of the hyperpolarizability value, therefore, lies in this direction. However, in the thiadiazole (**Ia**), oxadiazole (**Ib**) and triazole (**Ic**), there are two directions of charge transfer, one lies from left to right from donor to acceptor, but another lies from the bottom to the top of the molecule from either the sulfur, oxygen, or nitrogen atoms at the 1-position of the respective ring to the two nitrogens at the 3- and 4-positions. As a consequence, the overall dipole moment is the resultant of these two local dipoles and the hyperpolarizability which arises mainly from electron donation from the donor to the acceptor groups, is split into two components.

Conclusions

The *ab initio* 3-21G basis set appears to give a reasonable account of the geometry of all the heterocycles considered here by comparison with crystallographic data. The donor–acceptor 1,3,4-thiadiazole (**Ia**), 1,3,4-oxadiazole (**Ib**) and 1,3,4-triazole (**Ic**) all show much larger dipole moment changes than the corresponding thiophene (**If**), furan (**Ig**) and pyrrole (**Ih**) on excitation, but their calculated hyperpolarizabilities are smaller mainly because of their smaller transition moments.

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